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EFFECT OF ADDING LIQUID GLASS ON THE COMPACTION AND REACTIVE SINTERING OF CERMET Al_2O_3 – Al

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The salient features of the process of compaction and reactive sintering of Al_2O_3 – Al cermet compacts with additions of liquid glass are studied. The introduction of 3 – 28 wt.% glass into the initial aluminum powder, consisting of plate-shaped particles with aluminum-oxide surface films, yields granular material with bulk mass $0.4 – 0.5$ g/cm^3. The salient features of the compaction of granular powder are studied by analyzing logarithmic diagrams. It is shown that reactive sintering of samples in air occurs in a filtration combustion regime, and the dry residue of liquid glass activates sintering, resulting in the formation of γ-Al_2O_3, θ-Al_2O_3, α-$Na_2Si_2O_3$, and Si nanodispersed inclusions in an aluminum matrix with a layered structure. The flexural strength of $2.40 – 2.45$ g/cm^3 cermet is 300 – 320 MPa.

Aluminum-oxide – aluminum cermet is of technical interest because it combines the useful properties of the oxide and metallic phases which are present in it. For example, the high hardness characteristic of Al_2O_3 and the substantial plasticity with low density which are characteristic of aluminum make such a composite material promising for light structural elements with enhanced durability, crack resistance, impact viscosity, and resistance to fatigue failure. The well-known technological approaches used to obtain Al_2O_3 – Al cermet are based on permeation under pressure of aluminum melt into a porous aluminum-oxide framework, directed reactive permeation (Lanxide process), and "liquid stamping" of aluminum melt with aluminum oxide particles mixed in it and on the process of self-propagating high-temperature synthesis (US Patent No. 6183877) [1 – 3].

In a previous work we showed that such a cermet can be obtained by reactive sintering (RF Patents Nos. 2226516 and 2266270) [1], and we determined its physical and mechanical properties and possible areas of application [4]. In the present article we examine the salient features of the compaction and reactive sintering of Al_2O_3 – Al cermet compacts using additions of liquid glass.

Commercial grade PAP-2 aluminum oxide powder (GOST 5494–95) consisting of plate-shaped particles with predominant sizes $(10 – 100) \times (5 – 50) \times (0.5 – 1.0)$ μm

was used (Fig. 1). The powder was heat-treated for a short time in air in order to form the required amount of the aluminum oxide phase in the form of a thin film in the surface of each particle. Next, the powder was granulated in order to decrease the volatility of the dust-like fraction present in it and to increase the bulk mass in order to decrease the volume of the filling hopper. For this, liquid glass was used as a binder (a concentrated water solution of hydrated sodium silicate nNa$_2$O $\cdot$ mSiO$_2$ $\cdot$ χH$_2$O, where m/n is the modulus of the liquid glass and varies from 1 to 4 and χ varies from 1 to 14 depending on the degree of hydration). It was introduced into the aluminum powder, as a result of which the particles were glued together. The moist mixture obtained was passed
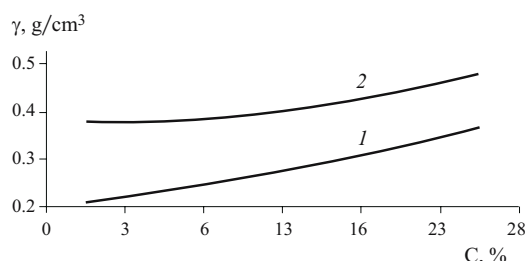

Fig. 1. PAP-2 aluminum powder particles ($\times$ 850).

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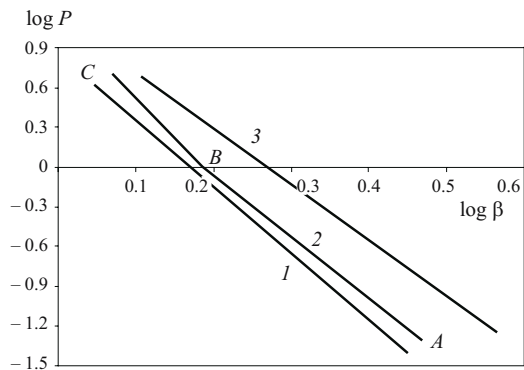**Fig. 2.** Granular aluminum powder after flowing out of the hopper (× 2).

Fig. 3. Bulk mass γ of granular aluminum powder versus the content C of dry residue of the liquid glass with free fill (1) and after shaking (2).

Fig. 4. Logarithmic powder compaction diagrams: 1) ungranulated aluminum powder (C = 0%, $m = 5.0245$, $y = -5.0245x + 0.8558$); 2) granular aluminum powder (C = 3%; $m = 4.6443$, $y = -4.6443x + 0.8657$ for the section AB; $m = 6.0367$, $y = -6.0367x + 1.1245$ for the section BC); 3) granular aluminum powder (C = 28%, $m = 4.2131$; $y = -4.2131x + 1.1325$).

through a sieve with 1.6 mm cells, after which the granular material was allowed to dry naturally. The general form of the granular powder (the content of the liquid glass was 3%[2] per the dry residue of the material) after leaving the hopper through a 7 mm in diameter opening is shown in Fig. 2 (the natural slope incline is approximately 45°).

The bulk mass γ of the granular aluminum powder in the form of a free fill and after it has been shaken increases monotonically as the amount of dry residue of liquid glass (DRLG) increases from 3 to 28% (Fig. 3). It changes from 0.26 to 0.37 g/cm³ in the first case and from 0.4 to 0.5 g/cm³ in the second case, while the bulk mass (after being shaken) of the ungranulated powder fluctuates in the range 0.15 – 0.2 g/cm³. Thus, the addition of liquid glass makes it possible to increase the bulk mass by more than a factor of 2. This substantially decreases the volatility of the dusty fraction present in the initial powder. This is very important when the die cavity of the compacting press is filled with the granular material.

It should be noted that the role of liquid glass is limited only to its binding capability with respect to the powder particles. It must also activate the reactive sintering process.

The granular powder fill was compacted in a steel compaction mold. In this case, the compaction is accomplished by plastic deformation of plate-shaped aluminum particles. We assume that under a load ruptures occur in their surface

aluminum oxide films and that covering of these ruptures promotes the appearance of local regions of contacts along a metallic phase (Al – Al) between the particles. Particles present in these regions become joined, as a result of friction, by the cold welding mechanism. Then the structure of the compacted blank consists of plate-shaped particles between which lies DRLG. We note that as its content decreases, the fraction of contacts ($Al_2O_3 - Al_2O_3$) directly along the surface aluminum-oxide films of the neighboring particles increases.

The salient features of the powder compaction process were studied by M. Yu. Bal'shin's method [5]. To this end, the relation

$$\log P = -m\log \beta + \log P_{\max},$$

where P is the applied pressure, m is the compaction ratio, $\beta = 1/\theta$ (θ is the relative density of the compact), and $P_{\max}$ is the compacting pressure which yields a nonporous compact, was used to construct curves in the ($\log \beta$, $\log P$) plane, which were then analyzed.

It is evident (Fig. 4, curves 2 and 3) that adding liquid glass to the aluminum powder decreases the density of the compact in the entire range of the applied compaction pressure (5 – 500 MPa) as compared with the density of the samples obtained from the powder without added glass (curve 1). This can be explained by the presence of DRLG, distributed over the surface of the plate-shaped powder particles and impeding the formation of a strong bond along their planes. Evidently, increasing the DRLG content will decrease the total area of all contacts along the metal phase (Al – Al) between the particles. In this case the lack of tight bonding of the plate-shaped particles along the planes will result in the formation of communicating slit-shaped air-filled pores in the compacting system, which is important for achieving effective reactive sintering.

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[2] Here and below, unless otherwise stated, the weight content.

It was also determined that for DRLG content 3% (curve *2*) the stiffness of the powder system loaded and, correspondingly, the compaction ratio estimated by the tangent of the slope angle of the straight line with respect to the abscissa change. Thus, it is likely that at the initial stage of compaction pressure application (section *AB* of the curve) the DRLG decreases the friction between the particles, acting as a dry lubricant. Here, the compaction ratio $|m|$ is less than for powder with no glass (curve *1*). Then, $|m|$ increases (the section *BC* of the curve) because the plasticity of the loaded system decreases as a result of the finely dispersed oxide particles, contained in the DRLG, present in it. As a result, the contact stresses increase. Similar curves were obtained when powders with up to 13% DRLG were compacted. When the amount of DRLG in powder is much larger (curve *3*) or there is no DRLG at all (curve *1*) the compaction ratio remains unchanged when load is applied; this indicates that the contact stresses are constant in the pressure range chosen for compaction.

Reactive sintering of samples compacted under pressure 500 MPa can be divided conventionally into two stages. Initially, it proceeds in the filtration combustion regime [3]. On heating in air at temperatures up to 600°C their surface ignites and a combustion front propagates into the interior volume. During this period air is sucked in through the system of communicating slit-shaped pores (filtration) as a result of the pressure drop between this gaseous oxidizer inside the pore space and around the compacted sample. The interaction of the aluminum with the oxygen in the air proceeds as a result of the diffusion of gas molecules to the metal phase through the surface aluminum oxide films and also through discontinuities — microcracks which are formed in them on heating. As a result of the exothermal aluminum combustion reaction, the brightness temperature of the surface of the blank, as shown by a pyrometric evaluation, is 700 – 800°C. Under these conditions aluminum exists in the form of a superheated (above the melting point) melt confined by aluminum-oxide surface films. The heat released during the exothermal reaction promotes sintering of the particles in the regions of contact $(Al_2O_3 - Al_2O_3)$ between their aluminum-oxide films. It is obvious that the stresses appearing as a result of the thermal expansion of the melt should not exceed the strength of these films or the strength of the aluminum-oxide framework formed as result of the combustion. Otherwise, melt will be ejected from the volume of the article.
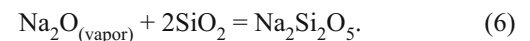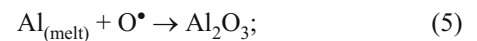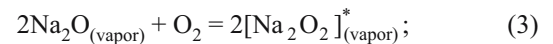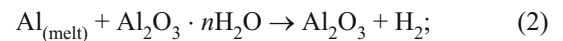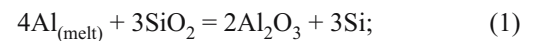
The sintered blank is no longer permeable to air after enough of the aluminum-oxide phase accumulates in its pores. Then filtration combustion is completed. At this moment a substantial fraction of unreacted metal remains in its volume. Next, at the last stage, DRLG plays the main role in the reactive sintering process.

In accordance with the phase composition of the sintered sample (vol.%) — 82 Al, 9 γ-Al_2O_3, 6 θ-Al_2O_3, 2 α-Al_2O_3, and 1 Si — with DRLG weight content 3%, furnace temperature 600°C, and isothermal soaking for 1 h, as determined
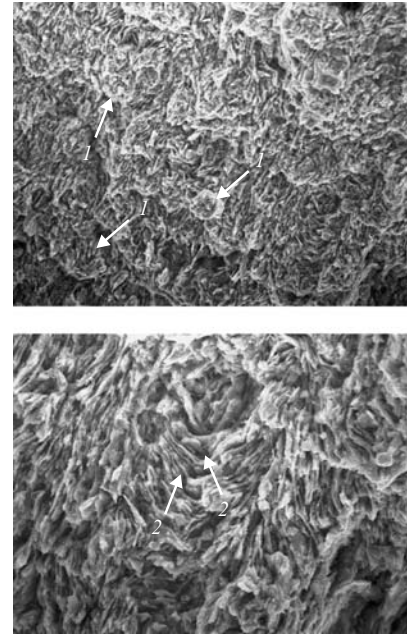
Fig. 5. Surface of discontinuity of reactively sintered $Al_2O_3 - Al$ cermet: *1*) granules ($\times$ 850); *2*) layers ($\times$ 1650).

from the surface of discontinuity by x-ray phase analysis and local x-ray spectral analysis, in can be conjectured that the following chemical reactions occur:

$$4Al_{(melt)} + 3SiO_2 = 2Al_2O_3 + 3Si; \qquad (1)$$

$$Al_{(melt)} + Al_2O_3 \cdot nH_2O \rightarrow Al_2O_3 + H_2; \qquad (2)$$

$$2Na_2O_{(vapor)} + O_2 = 2[Na_2O_2]^*_{(vapor)}; \qquad (3)$$

$$[Na_2O_2]^*_{(vapor)} \rightarrow Na_2O_{(vapor)} + O^{\bullet}_{(atomic)}; \qquad (4)$$

$$Al_{(melt)} + O^{\bullet} \rightarrow Al_2O_3; \qquad (5)$$

$$Na_2O_{(vapor)} + 2SiO_2 = Na_2Si_2O_5. \qquad (6)$$

The reaction (1) is exothermal. Accordingly, the reagents interact via the destruction of continuity in the aluminum oxide surface films on the aluminum particles. According to SPA, such films exist as a crystal hydrate. Consequently, it can be decomposed by the aluminum melt according to the reaction (2) with formation of an additional amount of the aluminum oxide phase, strengthening the surface films.

In our opinion, sodium oxide introduced into the powder via the liquid glass is a catalyst for the oxidation of aluminum. Its catalytic effect can be described as follows. At the filtration combustion stage Na_2O vaporizes as a result of heating and its vapors saturate the pore space of the compact. As a result of the higher oxygen affinity of sodium, an unstable peroxide complex forms according to the reaction (3). Decomposing via the reaction (4), it serves as a source of atomic oxygen, distinguished by an enhanced reactivity.

Atomic oxygen diffuses through the aluminum-oxide surface films to the aluminum melt, interacts with it, and forms Al_2O_3 crystals in accordance with the reaction (5). In addition, a sodium silicate compound forms as a result of the interaction of the oxide components of the liquid glass — the reaction (6).

It should be noted that the crystalline phases which are formed are nanodispersed inclusions (γ-Al_2O_3 — $13 - 20$, θ-Al_2O_3 — $25 - 100$, α-$Na_2Si_2O_3$ — $25 - 30$, Si approximately 100 nm). Figure 5 displays the general surface of discontinuity of the sintered material. It is characterized by a layered structure, which is formed from granules (1) consisting of plate-shaped particles. The joining of the layers (2) along the planes is accomplished by sintering. For the density of the present cermet $2.40 - 2.45$ g/cm^3 its flexure strength is $300 - 320$ MPa, which is 1.5 times higher than for reactively sintered Al_2O_3 – Al cermet without liquid glass added. The physical interpretation of this effect can probably be based on the formation of a dispersion hardened structure, capable of effectively braking the motion of dislocations, during the reactive sintering process.

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